

Anisotropic Spin–Lattice Relaxation of Deuterated Hexamethylbenzene

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The anisotropic spin–lattice relaxation of deuterated hexamethylbenzene (HMB- d_{18}) was measured at -36 and 70°C . The anisotropy is due to the anisotropic sixfold reorientation of the molecule about its hexad axis, and a model is presented to explain quantitatively the anisotropy, considering only single-particle relaxation. The temperature dependence of T_1 was measured, and the activation energy and correlation time for the sixfold reorientation were determined.

The hexamethylbenzene molecule in the solid state undergoes a reorienting motion about its hexad axis (C_6 motion) over a wide range of temperature as shown by second moment, T_1 , and $T_{1\rho}$ studies of the protonated material (1–3). As a consequence of this anisotropic C_6 reorientation the nuclear spin–lattice relaxation exhibits a strong dependence on the orientation of the molecular hexad axis with respect to the applied magnetic field (Fig. 1). We report here the T_1 anisotropy of a single crystal of deuterated hexamethylbenzene (HMB- d_{18}) measured on both sides of the T_1 minimum, and we present a model to explain the temperature dependence of this anisotropy.

In addition, from the measured temperature dependence of T_1 over the range -85 to 70°C the activation energy and correlation time for the C_6 motion are determined and compared with the previously reported values for the protonated compound.

THEORY

There are two motions associated with the hexamethylbenzene molecule. In addition to the aforementioned C_6 motion of the entire molecule, each of the six methyl groups undergoes rapid reorientation about its C_3 axis. The C_3 and C_6 reorientations cause fluctuations in the deuterium quadrupole interaction, and these quadrupole fluctuations are responsible for the deuterium spin–lattice relaxation. The spin–lattice relaxation is most efficient (T_1 minimum) when the rate of fluctuation is near the Larmor frequency. In the temperature range of our measurements the rate of the methyl group C_3 motion is much larger than the rate of the molecular C_6 motion and far away from the Larmor frequency. Consequently, it is a very good approximation to neglect the contribution to the spin–lattice relaxation by the fast C_3 motion. Since deuterium dipole–dipole coupling

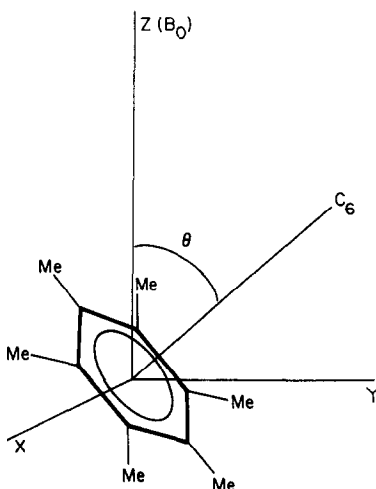


FIG. 1. Hexamethylbenzene- d_{18} molecule oriented in magnetic field with field direction along the z axis.

is much smaller than the quadrupole interaction, it is also legitimate to neglect the contribution (estimated to be less than 1%) of the fluctuating dipolar interaction to the relaxation.

Unlike the dipolar interaction, the quadrupole interaction is associated with a single nucleus. With this in mind and ignoring fluctuations due to the fast C_3 motion, the system of 18 deuterons can be simplified to the treatment of a single deuteron with a reduced quadrupole strength and principal axis along the methyl group C_3 axis. The Hamiltonian of this deuteron consists of a Zeeman term (H_z), a time-averaged truncated quadrupole term (\bar{H}_Q), and a fluctuating quadrupole term ($H_1(t)$) which is responsible for relaxation;

$$\mathcal{H} = H_z + \bar{H}_Q + H_1(t) = -\omega_0 I_z + \omega_Q (-1/2) P_2(\cos\theta) T^{(0)}/3 + H_1(t), \quad [1]$$

where $T^{(0)} = 3I_z^2 - I(I+1)$, ω_0 is the Larmor frequency, ω_Q the quadrupole frequency, and θ the angle between the molecular C_6 axis and the magnetic field (Fig. 1). The fluctuation term $H_1(t)$ can be expressed explicitly as a sum of products of tensor operators $T^{(m)}$ and time-dependent spatial functions $F^{(-m)}(t)$:

$$H_1(t) = \frac{\omega_Q}{3} \sum_{m=-2}^2 (-1)^m T^{(m)} F^{(-m)}(t), \quad [2]$$

where

$$F^{(0)} = \frac{3}{4} \cos 2\phi \sin^2 \theta,$$

$$F^{(1)} = -i \frac{6^{1/2}}{8} \cos 2\phi \sin 2\theta - \frac{6^{1/2}}{4} \sin 2\phi \sin \theta,$$

$$F^{(2)} = -\frac{6^{1/2}}{8} \cos 2\phi (1 + \cos^2 \theta) + i \frac{6^{1/2}}{4} \sin 2\phi \cos \theta,$$

and

$$F^{(-m)} = (-1)^m (F^{(m)})^*$$

$F^{(0)}$ is included for completeness although it does not contribute to T_1 relaxation.

The time dependence of $F^{(m)}$ is continued in the randomly fluctuating angle ϕ which describes reorientation of the molecule about its C_6 axis with correlation time τ_c . Since all of the time dependences enter into $H_1(t)$ as 2ϕ , only one correlation time is necessary to describe the relaxation. With one correlation time it is impossible to distinguish sixfold reorientation from rotational diffusion (4). However, X-ray analysis shows that the hexamethylbenzene molecules do have specific sixfold equilibrium orientation (5). Thus, τ_c may be viewed as an inverse jumping rate.

In general the relaxation of a multispin system must be described by a relaxation matrix S (6). Since our treatment involves only single-particle relaxation, the spin-lattice relaxation rate (i.e., $1/T_1$) is given by the single matrix element S_{11} which we have evaluated to be

$$S_{11} = 6J^{(1)} + 24J^{(2)}, \quad [3]$$

where $J^{(1)}$ and $J^{(2)}$ are the spectral densities

$$J^{(1)} = \left(\frac{\omega_Q}{3}\right)^2 \frac{3}{16} (1 - \cos^4 \theta) \frac{\tau_c}{1 + \omega^2 \tau_c^2},$$

$$J^{(2)} = \left(\frac{\omega_Q}{3}\right)^2 \frac{3}{64} (1 + 6 \cos^2 \theta + \cos^4 \theta) \frac{\tau_c}{1 + 4\omega^2 \tau_c^2}.$$

The dependence of $T_1(S_{11}^{-1})$ upon the angle θ is evident from the spectral densities. T_1 has a minimum for the C_6 axis parallel to the magnetic field and increases monotonically as θ increases up to 90° . The anisotropy of T_1 depends on the temperature since τ_c is temperature dependent (Fig. 2). It is interesting to note that the spectral density $J^{(1)}$ vanishes when the C_6 axis is parallel to the applied magnetic field, meaning that only $J^{(2)}$, corresponding to double quantum transitions, contributes to the relaxation at this orientation.

EXPERIMENT AND DISCUSSION

All experiments were performed using a single crystal of HMB- d_{18} . This greatly facilitates the study of the anisotropic spin-lattice relaxation since all molecular C_6 axes are parallel in the single crystal (4). T_1 was measured using a saturation-recovery pulse sequence (i.e., $(90^\circ - \tau')_n - \tau - 90^\circ$, $T_2 \ll \tau' \ll T_1$) in a field of 25.8 kG with a corresponding deuterium resonance frequency of 16.8 MHz.

The angular dependence of the spin-lattice relaxation rate S_{11} was measured at two temperatures, -36 and 70°C . The results are shown in Fig. 2. With the single crystal oriented so that all of the molecular C_6 axes are parallel to the field, (i.e., $\theta = 0$), the temperature dependence of S_{11} was measured over the range -85 to 70°C . The observed temperature dependence is shown in Fig. 3.

For the single orientation of the C_6 axes parallel to the field only the second term

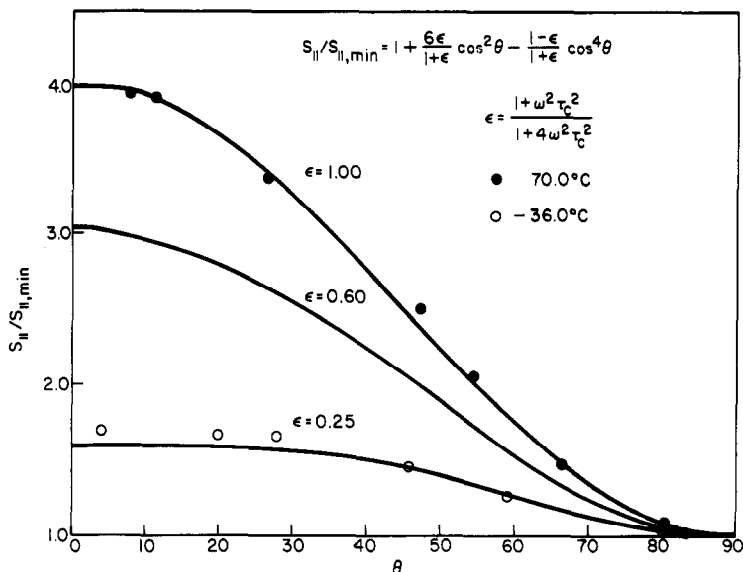


FIG. 2. The angular dependence of the spin-lattice relaxation rate at two temperatures (-36 and 70°C) is shown along with the theoretical fit (solid line) for three different values of the parameter ϵ defined in the figure. $\epsilon = 0.25$, corresponding to the low temperature limit (i.e., $\omega^2\tau_c^2 \gg 1$) and $\epsilon = 1.00$, corresponding to the high temperature limit (i.e., $\omega^2\tau_c^2 \ll 1$).

($J^{(2)}$ term) in Eq. [3] is expected to contribute to the relaxation:

$$S_{11} = A \frac{c}{1 + 4\omega^2\tau_c^2} \quad [4]$$

Assuming an Arrhenius form for the correlation time,

$$\tau_c = \tau_{c0} \exp(E_a/RT),$$

the data are best fitted to the above expression for S_{11} with the values

$$A = (6.1 \pm 0.1) \times 10^{10} \text{ sec}^{-2},$$

$$\tau_{c0} = (1.8 \pm 0.3) \times 10^{-15} \text{ sec},$$

$$E_a = 7.8 \pm 0.1 \text{ kcal/mole},$$

where E_a is the energy of activation needed for the molecule to reorient about its C_6 axis. The theoretical fit of the data is shown in Fig. 3. The deviation of the theoretical fit from the data at low temperature may be due to our neglect of the methyl-group rotation (C_3 motion) which becomes increasingly important at low temperature.

Our measured activation energy for HMB- d_{18} is substantially higher than the reported value (6.7 ± 0.1 kcal/mole) for the fully protonated HMB. Viewing the molecule as a torsional oscillator sitting in a sixfold well, the activation energy for reorientation is expected to increase upon deuteration. Deuteration increases

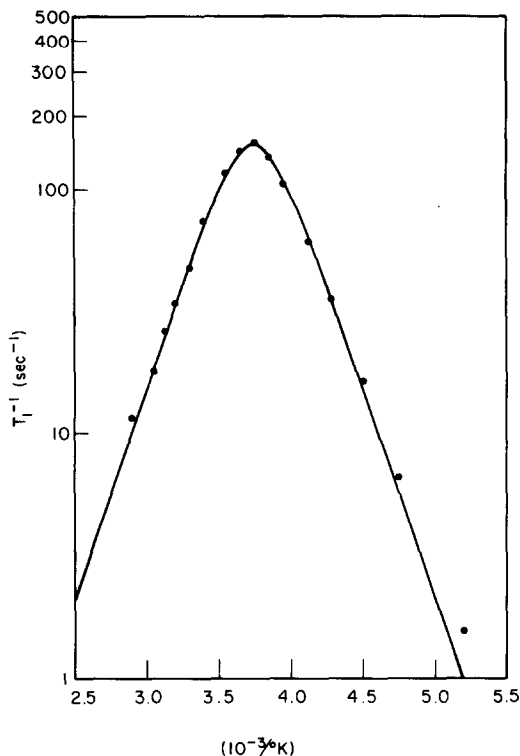


FIG. 3. Temperature dependence of the spin-lattice relaxation rate for the HMB- d_{18} single crystal oriented with all molecular C_6 axes parallel to the magnetic field. The solid curve is the best fit of Eq. [4] to the data.

the moment of inertia of the molecule, thus shifting the torsional energy levels down and increasing the spacing between zero-point energy and barrier top.

From the value of A given above the effective quadrupole strength is found to be $\nu_{Q,eff} = 39.1 \pm 0.3$ kHz, which agrees quite well with our measurement of the powder pattern at -170°C , where the C_6 motion is essentially frozen, $\nu_{Q,-170^\circ\text{C}} = 38.2 \pm 0.4$ kHz. This agreement indicates that it is valid to consider only the methyl-group-averaged quadrupole strength as contributing to the relaxation.

There is a problem, however, in comparing the effective quadrupole strength with the powder pattern value for HMB- d_{18} at room temperature. At room temperature where the C_6 motion is rapid the powder pattern value is expected to be exactly one-half of the effective quadrupole strength. In fact, the measured value is $\nu_{Q,25^\circ\text{C}} = 16.6 \pm 0.2$ kHz, which is about 15% smaller than expected. One explanation for this reduced value is that there is some additional motion besides in-plane reorientation of the molecule. One possibility is that the molecule is not constrained to lie in a plane, but rather its C_6 axis can rock about in a cone. Such out-of-plane motion seems unlikely since measurements of C^{13} chemical shielding anisotropy in HMB do not indicate any significant change in σ_{33} over the temperature range -186 to 23°C (7). The quantity σ_{33} is the element of the chemi-

cal shielding tensor corresponding to a principal axis perpendicular to the molecular plane. Additionally, $T_{1\rho}$ measurements which are sensitive to slow motion have not indicated the existence of any motion other than C_6 motion.

An alternate explanation is that the principal axis of the quadrupole interaction of a CD_3 group is not perpendicular to the molecular C_6 axis. This is possible if the three deuterons of the CD_3 group experience different local electric field gradients so that when averaged over the C_3 motion the effective quadrupole axis lies outside the molecular plane. For a free C_3 rotor the average could never be out of plane, but in HMB, where there are many methyl–methyl steric interactions the methyl groups may be staggered in such a way that some groups give above-plane averages while others give below-plane averages.

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